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SEASONAL DYNAMICS OF HEAVY METAL POLLUTION OF NIGER DELTA RIVER SEDIMENT RECEIVING INDUSTRIAL EFFLUENTS

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ABSTRACT
The heavy metal changes of Okpoka-Woji River serving as a sink of effluent of industries located in its vicinity within the Trans Amadi Industrial area were monitored over rainy and dry season months in order to follow the seasonal dynamics engendered by the dumping. Sediment samples from six sampling stations located along the river were collected for the determination of heavy metals. The mean values for the heavy metals were as follows: lead ranged from 17 - 67.2 mg/kg and 22.3-67.8 mg/kg; iron 7,995.5 - 17024.2 mg/kg and 6949.3 - 21,403 mg/kg; chromium 0.8-2.3 mg/kg and 16-3.4 mg/kg; Zinc 3195.1 - 4455.5 mg/kg and 1713.4-3417.3 mg/kg; manganese 22.5 - 100.6 mg/kg and 20.8 - 121.7 mg/kg; nickel 2.4 - 9.2 mg/kg and 2.0-6.9 mg/kg; vanadium 25.6 - 42.2 mg/kg and 26.1- 50.2 mg/kg; copper 19.5 - 46.9 mg/kg and 36.7 - 67.5 mg/kg; cadmium 0.3 - 1.6 mg/kg and 0.8 - 1.6 mg/kg; barium 21.1 - 77.6 mg/kg and 22.6 - 34.0 mg/kg respectively for the rainy and dry season months. These results showed that seasonal changes as well as industrial effluent discharges influenced the heavy metal values of the river.

KEYWORDS: Seasonal dynamics, heavy metals, pollution, industrial effluents, sediment.

INTRODUCTION

A pollutant is a substance that occurs in the environment at least in a part as a result of human activities and which has a deleterious effect on the environment (Moriarty, 1990). Pollutants are now unfortunately part of our environment as a result of industrial and other sources. There have been substantial increases in the industrial and agricultural development in the Niger Delta with the attendant population growth. These activities have resulted in the direct discharge of organic and inorganic substances including crude oil and refined products through normal operations (effluents), operational failures and sabotage to facilities into the adjoining water bodies. Other times as these components get into the water body, they finally settle at the sediment which acts as sinks of contaminants in aquatic systems (Chindah *et al*., 2004; Muncha *et al*., 2003).

Sediments are important substrates for heavy metals attachment in any aquatic environment (Horowitz, 1985; Deely *et al*., 1992). The degree to which water systems withstand heavy metal pollution is frequently dependent on the concentration of suspended sediment in the water column. Suspended sediment in the water particularly clay (< 4 μm) act as sponges adsorbing metals directly from the dissolved settles, the bottom sediment will build up a record on metal pollution in an area (Cauwet, 1987; Forstner, 1989).

Sediment is composed of a combination of lithogenic, antigenic and biogenic components such as mineral grains, organic matter, iron and manganese oxides, sulphides and carbonates. Heavy metals may be attached to any of these phases in proportions, which depend on the physicochemical conditions prevailing in the sediment and associated water. It has been seen that as the grain size decreases, the concentration of metals adsorbed onto sediment component increases particularly across the transition zone from silt to clay. The flat platy structures of clay minerals have high surface areas, surface charges and cation exchange capacities, which readily attract metals and metals carrying substrates (Forstner and Wittmann, 1981; Horowitz, 1985; Cauwet, 1980; Deely *et al*., 1992)

Various heavy metals other than mercury including tin, cobalt, chromium, nickel, cadmium and thallium are used in metal alloys or as catalysts. Their mining, smelting and ultimate disposal causes heavy metal pollution

problems. All these metals are substantially toxic to plants, animal and many microorganisms (Atlas and Bartha, 1993).

The trace metals that enter the aquatic environment from both natural and anthropogenic sources may be as a result of direct discharge into both fresh water and marine ecosystem or through indirect routes such as dry and wet deposition and land runoff. The important natural sources include coastal supply such as rivers, glaciers wave action and erosion; deep sea supply which included volcanic activities, tectonic activity and chemical processes in sediment and atmospheric mainly particles and vapours (mercury). The anthropogenic sources include direct processes such as mining, smelting and refining and indirect processes, which include electroplating catalysts and petrochemical industry. Other atmospheric sources include fossil fuel burning (Kiely, 1998).

The aim of this work is therefore to determine the effect of season on the heavy metal of the river receiving industrial effluents.

MATERIALS AND METHODS

Study area

The Okpoka-Woji River is situated in the coastal environment of the Niger Delta Rivers State, Nigeria. It arises from the bifurcation to the left of the Okpoka River, which drains into Bonny River. The area has a mean water depth of 4.8m, which is tidal and gradually transits from fresh to salt water at the head. The freshwater biotope flows unidirectionally downstream from the Rumuodara swamp forest transversing Port Harcourt - Aba express road bridge through Rumuogba (Mini-Okoro Police Station) where tidal effects begin, hence the beginning of the incursion of salt water (Figure 1).

Collection of sediment samples

Sediment samples were collected from the river at the discharge point once in a month from April 2001 - March 2002. The sediment samples were collected using soil grab and were put in sterile black polyethylene bags. All the samples were analyzed immediately on reaching the laboratory.

Chemical Reagents

The chemical reagents used in the study were of analytical grade and were products of BDH Chemicals, Pooles, England; Sigma Chemical Company, St. Louis, Missouri, USA and Hach Company Ltd, Colorado, USA.

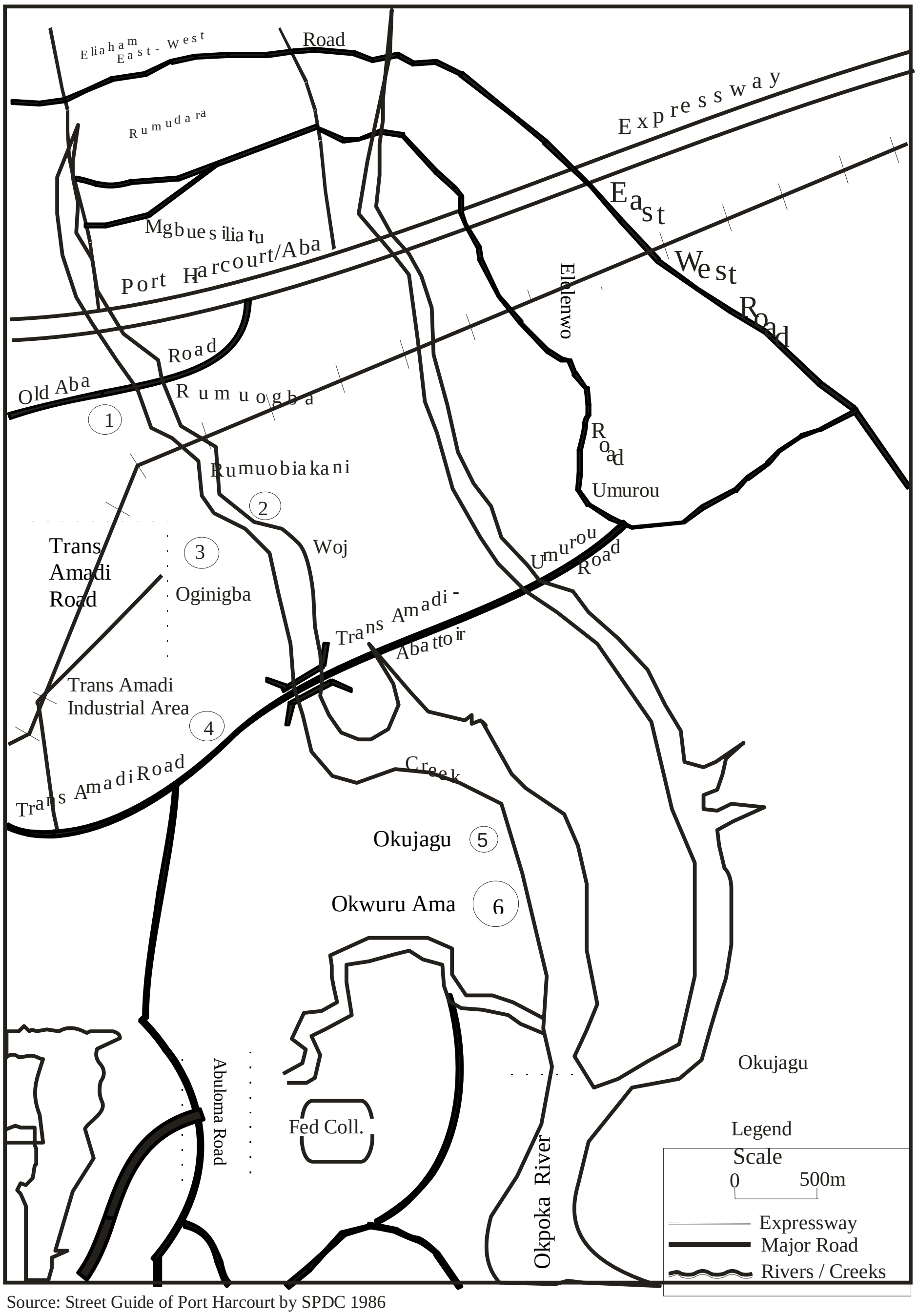
Heavy Metal Analysis

The sediment samples were air dried for 5 days and sieved with a sieve size of 1.70mm. The samples were digested using the methods adapted from ASTM (2003). This was done by weighing accurately 1g of the sieved sample, which was placed in the digestion container. Exactly 10ml of water, 5ml, HCL (S. G. I. 19) and 1ml of HNO_3 (S.G.I. 42) were added and swirled gently to mix. The containers were loosely capped and placed in a rack, which was then put in an autoclave. The samples were autoclaved for 30 minutes at 121^o C and 15 psi. The digestion containers were then removed from the autoclave and allowed to cool at room temperature. The contents of the digestion containers were quantitatively transferred to a 100ml volumetric flask and made up to volume with distilled water. The digests were analysed for heavy metals using atomic absorption spectrophotometer Model 969, Unicam. The statistical methods used were ANOVA and standard deviation. The determination was done three times.

RESULTS

The seasonal changes in the heavy metal contents of the Okpoka-Woji River sediment are shown in figures 2a to 4b. The mean values for lead, iron chromium and zinc where shown in Figures 2a - 2d. The mean value ranges were lead, 17 - 67.2 mg/kg and 22.3 - 67.8 mg/kg; iron, 7,995.5 - 17024.2 mg/kg and 6949.3 - 21,403 mg/kg; chromium, 0.8 -2.3 mg/kg and 1.6 - 3.4 mg/kg; zinc, 3195.1 - 4455.5 mg/kg respectively for rainy and dry season months. The mean values for lead, iron and chromium were observed to be higher in the dry

season month and rainy season month. Statistically the ANOVA $P < 0.05$ showed that there was significant difference in the mean values between the dry and rainy season months. The mean value for zinc was higher in the rainy season months than in dry season months. But statistics showed that there was no significant difference in the mean values between the rainy and dry season months as $P > 0.05$.



Source: Street Guide of Port Harcourt by SPDC 1986

Fig.1: Map of Woji Creek showing the sampling stations

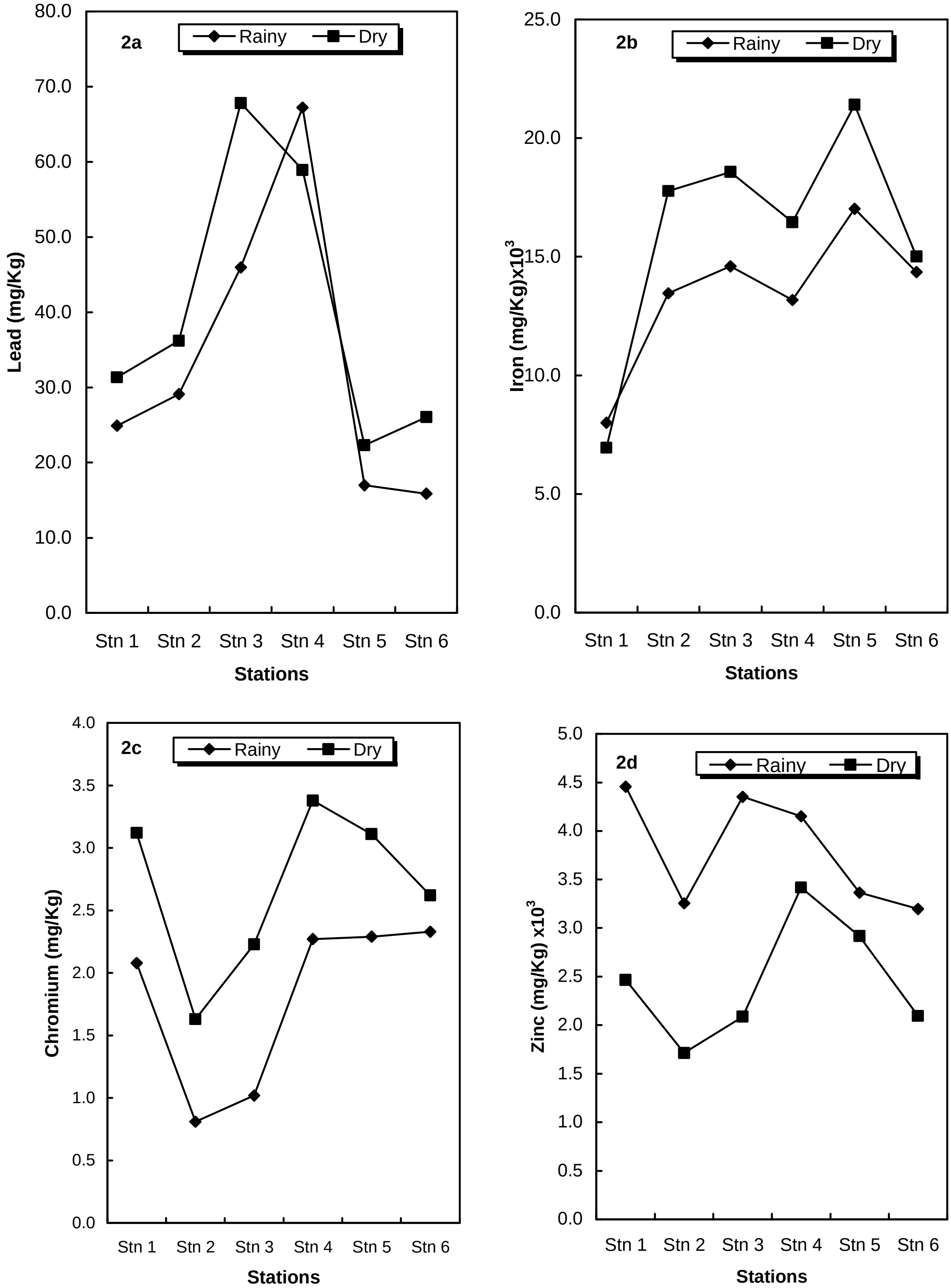


Fig. 2: Changes in the monthly mean values of lead, iron chromium and zinc levels of Okpoka-Woji River sediment across the stations.

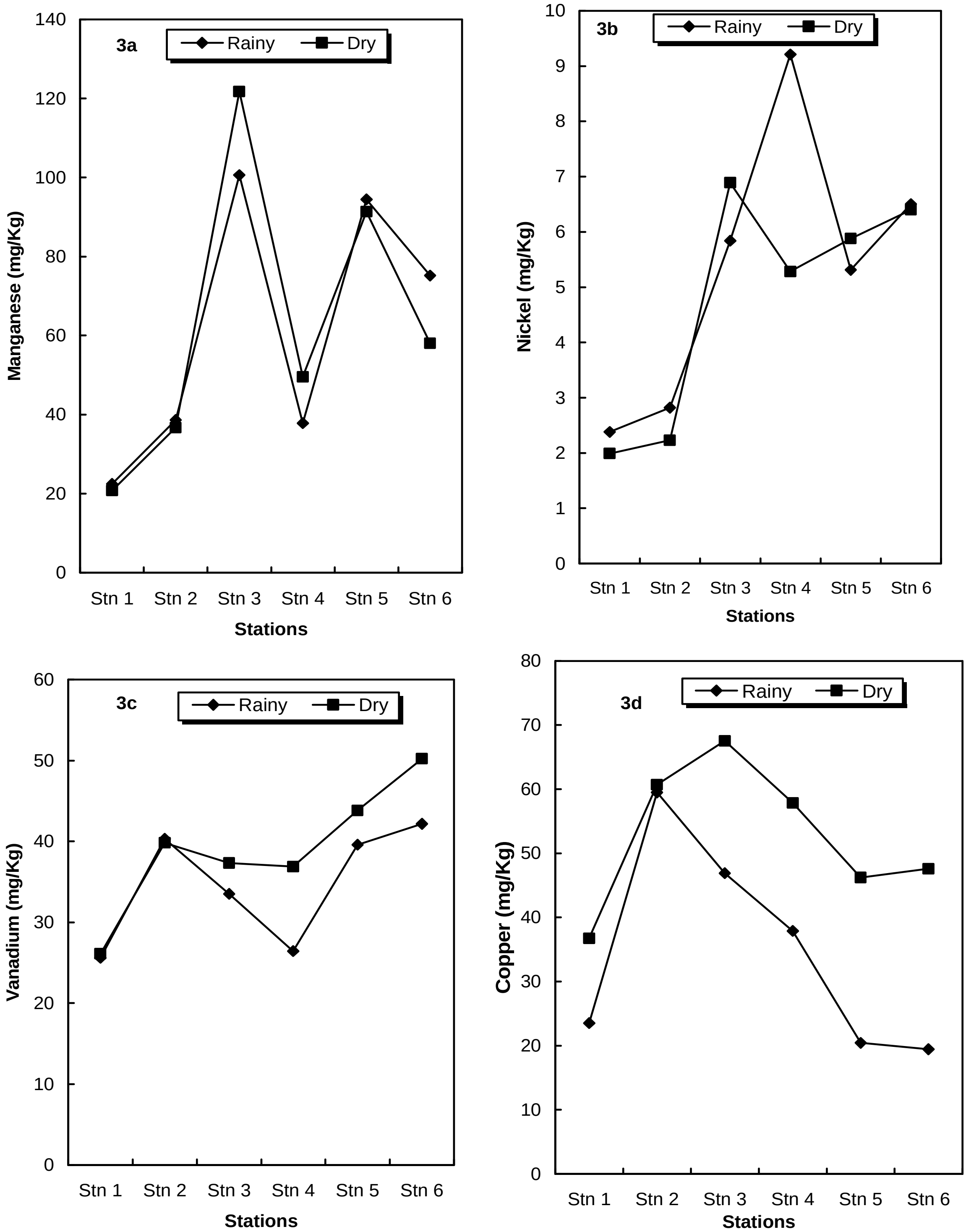
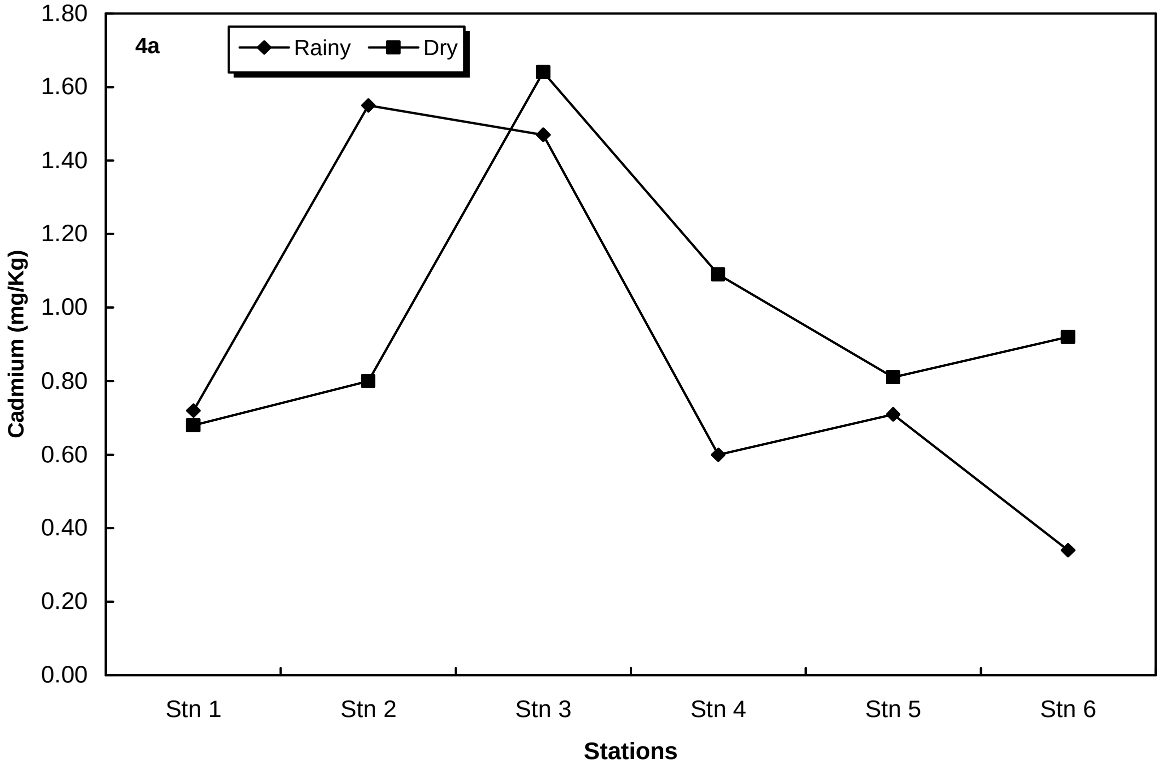


Fig. 3: Changes in the monthly mean values of manganese, nickel, vanadium and copper levels of Okpoka-Woji River sediment across the stations.



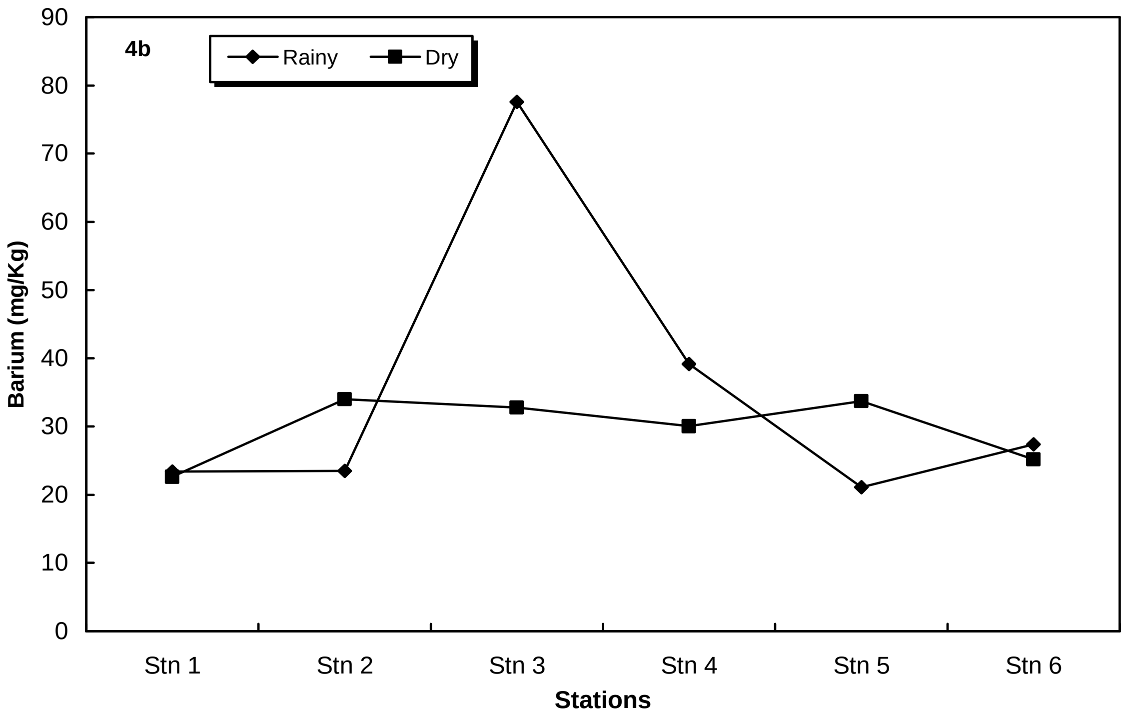


Fig. 4: Changes in the monthly mean values of cadmium and barium levels of Okpoka-Woji River sediment across the stations.

Figures 3a - 3d show the mean values for manganese, nickel, vanadium and copper. They had the following mean values ranges manganese, 22.5 - 100.6 mg/kg and 20.8 -121.7 mg/kg; nickel, 2.4 - 9.2 mg/kg and 2.0 - 6 mg/kg; copper, 19.5 - 46.9 mg/kg and 36.7 - 67 mg/kg respectively for rainy and dry season months. It was observed that the mean values were higher in the dry season months for manganese, vanadium and copperwhile the mean values for nickel were higher in the rainy season month than the dry season months. It was also observed that $P < 0.05$ showed that there was significant difference in the mean values between the dry and rainy season months for manganese, nickel and vanadium while $P > 0.05$ showed no significant difference in the mean values between the dry and rainy season months for copper.

The mean values for cadmium and barium are shown in Figures 4a - 4b. The mean values ranges were cadmium, 0.3 - 1.6 mg/kg and 0.8 - 1.6 mg/kg; barium 21.1 - 77.6 mg/kg and 22.6 -34.0 mg/kg respectively for the rainy and dry season months. It was observed that there was no significant difference in the mean values between the dry and rainy season months for cadmium and barium as $P> 0.05$.

DISCUSSION

The accumulation of heavy metals in sediments may become the re-pollution source for an aquatic environment when environmental changes occur. The levels of the heavy metals observed in the sediments during the study period were higher than those encountered in the surface water. The trace metal content of recent sediments depends on the anthropogenic inputs as well as the natural characteristics of the sediments especially in the grain size (Tkalin *et al*., 1996; Presley *et al*., 1992). The domestic and industrial effluents discharge may be implicated in the high concentration of the heavy metals observed. Okoye *et al.* (1991) reported anthropogenic heavy metal environment of Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn in the Lagos Lagoon and implicated land based urban and industrial wastes. Kakulu and Osibanjo (1988, 1992) revealed elevated levels of Pb, Cr, V and Zn in Port Harcourt and Warri sediments, which suggest that effluents from petroleum refineries located in these cities, have contributed significantly to the heavy metal pollution of the respective aquatic ecosystems.

The high concentrations of these heavy metals call for a serious concern in relation to ecological and human health. Contaminated sediment can be associated with acute and chromic effects on aquatic life. Sediment also constitute a major source of persistent bioaccumulative toxic chemicals which may pose threats to ecological and human health even after contaminants are no longer released from point and non-point sources. Adverse ecological effects of contaminants in sediment include fin rot skin lesions, increased tumor frequency and reproductive toxicity in fish, reproductive failure in fish eating, birds and mammals and decreased biodiversity in aquatic ecosystem. Threat to human health occurs when sediment contaminants bioaccumulate in fish and shellfish tissues consumed by humans (Armitage, 1997).

The seasonal dependent variation in the sediment of the heavy metals may be associated with seasonal factors such as nature of the sediment and runoff and water quality (Bryan, 1973; Szefer *et al.,* 1999). It was observed that zinc, nickel, barium had mean values higher in the rainy season months than the dry season months. The other metals studied namely lead, iron, chromium, manganese, vanadium, cadmium and copper had mean values higher in the dry season than in the rainy season months. The means, that there is much concentration of organic and inorganic nutrients in the sediment in the dry season than rainy season months. It also shows that the river water is cleaner in the rainy season dilution of industrial wastes as they enter river from rainfall, soil erosion and runoff.

This was in contrast with the findings of Chindah *et al*. (2004) and Biney (1997) who reported consistent higher concentration of zinc and copper in the dry season than in the dry season months while the rest of the metals higher mean values in the rainy season than dry season months. The mean values for nickel and barium were in agreement with their findings as the values were higher in the rainy season than dry season months.

Iron is used in steel production and is a byproduct of combustion and such it is expected to be present in large quantities. However, it is also found in many primary and secondary minerals in a significant weight, so the

increases are not necessarily anthropogenic in nature. It is certainly possible that the noted increase explained as deriving from anthropogenic emissions may to some extent be due to the diagenetic inputs (Varekamp, 1990).

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REFERENCES

Armitage, T. (1997). Contaminated sediment. *In: Proceeding of the U.S. Geological Survey (USGS) Sediment Workshop February 4-7, U.S. Environmental Protection Agency*

ASTM (2003). Standard practices for extraction of trace elements from sediments, Annual book of ASTM Standards vol. 11.02.

Atlas, R.M. and Bartha, R. (1993). *Microbial Ecology Fundamentals and Applications* , 3rd edition. The Benjamin/Cummings Publishing Company Inc. 390 Bridge Parkway, Redwood City, CA94065.

Bryan, G.W. (1973). The occurrence and seasonal variations of trace metals in the scallops *Pecten maximus* L. and *Chlamys opercalon* L., *Environmental Pollution*; 74: 227- 244.

Cauwet, G. (1987). Influence of Sedimentological Features on the Distribution of Trace Metals in Marine Sediments *Marine Chemistry*; 22.221-234

Chindah, A. C., Amabaraye, S. B. Amd Sibeudu, O. C. (2004). Distribution of Hydrocarbons and Heavy Metals in Sediment and A Crustacean (Shrimps - *Penaeus notialis)* from the Bonny/New Calabar River Estuary, *AJEAM-RAGEE*; 9:1-17.

Deely, J. M. Tunnicliff, J. C., Orange, C. J. and Edgerley, W.H.L. (1992). Heavy Metals in Surface Sediments of Waiwhetu Stream, Lower Hutt, New Zealand, *New Zealand Journal of Marine and Freshwater Research. 26:417-427*.

Forstner, U. (1989) *Contaminated Sediments: Lectures on Environmental Aspects of Particle Associated Chemicals in Aquatic Systems*, Berlin, Heidelberg, New York Springer-Verlag, pp 157.

Forstner, U., Wittmann, G.T.W. (1981). Metal Pollution in the Aquatic Environment, 2nd Edition, Berlin, Hedelberg, New York, Spriner-Verlag, pp 486

Horowitz, A.J. (1985). A Primer on Trace Element-sediment. Chemistry, U.S. Geological Survey water supply paper 2277, pp 6.7

Kakulu, S.E. and Osibanjo O. (1988). Trace Heavy Metal Pollutional Studies in Sediments of the Niger Delta Area of Nigeria, *Journal Chemical Society Nigeria*; 13; 9 - 15.

Kakulu, S.E. and Osibanjo O. (1992). Pollution Studies in Nigeria Rivers: trace metal levels of surface waters in the Niger Delta Area of *International Journal of Environmental Studies*; 41: 287 - 92.

Kiely, G. (1998). *Environmental Engineering*, International Edition, Mdiraw-Hill. International Limited, London, U.K.

Moriarty, F. (1990). *Ecotoxicology, A Study of Pollutants in The Ecosystem*, 2nd Edition, Academic Press London.

Muncha, A. P., Vassconcelos, M. T. S. D. and Bordalo, A. A. (2003). Macrobenthic Community in the Douuro Estuaryi Relation with Trace Metals and Natural Sediment Characteristics, *Environmental Pollution*; 121:169-180.

Okoye, S.C.O., Afolabi, O. A. and Ajao, E.A. (1991). Heavy Metals in the Lagos - Lagoon Sediments, *International Journal of Environmental Studies*; 37:35-41.

Presley, B.J., Taylor, R.J. and Boothe, P.N. (1992). Trace metal contamination in sediments of the Eastern Mississippi Bight, *Marine Environmental Resources*; 33: 267 -82.

Shell Petroleum Development Company (SPDC), (1986). Street Guide of Port Harcourt

Szefer, R., Wolowiez, M., Kusak, A., Desluus-Paoli, M., Garowski, W., Frelek, K. and Belzunce, M.J. (1999). Distribution of mercury and other trace metals in the cockir *Cerastoderma glaucum* from the Mediterranean Lagoon, *Etung De Thau. Arch Environmental Contamination Toxicology*; 36: 56 – 63.

Tkalin, A.V., Presley, B.J. and Boothe, P.N. (1996). Spatial and temporal variations of trace metals in bottom sediments of Peter the Great Bay, The Sea of Japan, *Environmental Pollution* ; 92: 73 – 78.

Varekamp, J.C. (1990). Trace Element Geochemistry and Pollution History of Mudflat and Marsh Sediment from the Connecticut Coastline, Weslsyen University E& ES Department.

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